Fuel 232 (2018) 36–44

Contents lists available at ScienceDirect

Fuel

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Full Length Article

The synergistic effect of Ni promoter on Mo-S/CNT catalyst towards hydrodesulfurization and hydrogen evolution reactions

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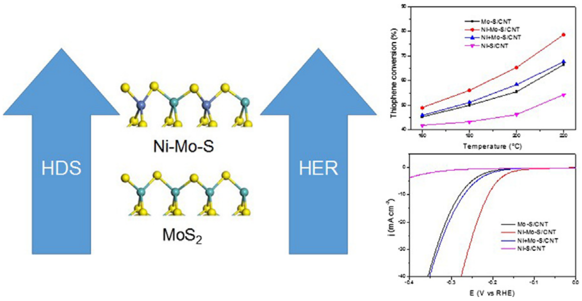
GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
MoS_2
Hydrodesulfurization
Hydrogen evolution reaction
Catalyst
Clean fuel

ABSTRACT

The effects of Ni promoter on Mo-S/CNT catalyst towards hydrodesulfurization (HDS) and hydrogen evolution reactions (HER) were studied. Ni promoter was introduced into Mo-S/CNT catalyst by one-step or mechanical mixing method, and Ni species presented in the form of Ni-Mo-S or Ni_3S_4, respectively. Catalytic assessments indicated that Ni-Mo-S structure had obviously better HDS and HER activities than MoS_2 at the same time, while Ni_3S_4 could not improve the activity of MoS_2 towards HDS or HER. The density functional theory (DFT) was also used to simulate and calculate the activation energies needed for HDS and HER on MoS_2 structure and Ni-Mo-S structure, respectively. It was found that the required activation energies for C–S bond breaking and H_2 generation on Ni-Mo-S structure were both significantly lower than that of MoS_2 structure. Therefore, it was proved theoretically that compared with MoS_2 structure, Ni-Mo-S structure had better catalytic activities for both HDS and HER.

1. Introduction

Industrial civilization brings convenience to human life, but also triggers a series of environmental problems, and the pollution of petroleum fuel combustion is particularly prominent [1,2]. The responses to this challenge lie mainly in the production of clean fuels and the search for alternative new energy sources [3,4]. At present, most of the world's energy supply comes from petroleum, which will continue to be an important global energy source in the near future [5]. Hydrodesulfurization (HDS) is the most widely used technique to remove

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https://doi.org/10.1016/j.fuel.2018.05.107
Received 12 December 2017; Received in revised form 20 April 2018; Accepted 22 May 2018
0016-2361/ © 2018 Published by Elsevier Ltd.

sulfur from petroleum and petroleum processing products, and molybdenumdisulfide (MoS_2) based materials are extensively used as HDS catalysts in refineries worldwide [6,7]. Hydrogen has been vigorously pursued as a promising alternative to traditional fossil fuels [8,9]. The electrocatalytic hydrogen evolution reaction (HER) is considered as one of the most important pathways for hydrogen production, and MoS_2 has also been extensively studied as a catalyst for HER [10,11].

It is interesting that MoS_2, which is always be considered as HDS catalyst, has also been proved to be good HER catalyst [12,13]. At present, researchers have begun to study the common points between the catalysis of HDS and HER. Some recent studies researched the connections between HER and HDS, observing that the edge sites (Mo atoms with sulfur vacancies) of MoS_2 that are active for HDS have also been proposed as the active sites for HER [14–17]. Furthermore, Saric et al. [18] used DFT to compare the energies of hydrogen adsorption under the conditions of HER and HDS, and found that HER and HDS reactions shared hydrogen as surface intermediate, thus having a common and elementary step which indicates that the same catalyst could perform well for both HER and HDS. After that, Saric et al. [19] built the equilibrium structure of the edge, corner and basal plane of an ideal CoMoS particle and found that edge and corner were active for both HDS and HER, while basal plane was inert for these two reactions. In our previous work [20], MoS_2 catalysts with different amounts of edge sites were synthesized. It was found that the HDS and HER catalytic activities were both in proportional to the amount of edge sites, which indicated that the active sites for HDS and HER on MoS_2 were highly consistent_ENREF_16 and MoS_2 with more edge sites would have better HER and HDS activities at the same time.

For HDS, it is widely accepted that Ni promoter can significantly improve the catalytic activity of MoS_2 [21]. Therefore, we are curious that whether the Ni promoter can also improve the HER catalytic activity of MoS_2 and in which form Ni promoter can improve the activity. In this work, Ni promoter was introduced into the Mo-S/CNT catalyst by different methods and the effects of Ni-Mo component distribution on HDS and HER activities were studied. HDS and HER catalytic assessments both indicated that only Ni-Mo-S structure had obviously better HDS and HER activities than MoS_2. In addition, DFT was used to simulate and calculate the activation energies needed for HDS and HER on MoS_2 structure and Ni-Mo-S structure, respectively, and the reason why Ni-Mo-S structure had better HDS and HER activities was discussed.

2. Experimental section

2.1. Catalyst preparation

High quality carbon nanotubes (CNTs) were purchased from XFNANO Materials Tech Co. and used as catalyst support in this work. Raw CNTs were purified by concentrated HNO_3 at 373 K for 3 h to increase the concentration of oxygen-containing functional groups, which were beneficial to the absorption of active metals. The filtered CNTs were thoroughly washed with deionized water and dried at 120 °C for 12 h for further use.

A series of CNT-supported catalysts were prepared by pore volume impregnation method. Typically, Ni-Mo/CNT catalyst with 12 wt% MoO_3 and 2 wt% NiO (Ni/Mo molar ratio = 0.32) was prepared by impregnating functionalized CNTs with an aqueous solution contained required amount of ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24}\cdot 24H_2O$) and nickel nitrate ($Ni(NO_3)_2\cdot 6H_2O$). Then the impregnated materials were dried at 120 °C overnight and calcined at 300 °C for 3 h in N_2 atmosphere. Analogously, Mo/CNT catalyst with 12 wt% MoO_3 and Ni/CNT catalyst with 2 wt% NiO were prepared by impregnating CNTs with $(NH_4)_6Mo_7O_{24}\cdot 24H_2O$ or $(Ni(NO_3)_2\cdot 6H_2O$ solution, respectively. In addition, Mo/CNT and Ni/CNT catalyst with higher loading were separately prepared and proportionally mixed to make a mixed catalyst with 12 wt% MoO_3 and 2 wt% NiO, and named as Ni + Mo/CNT.

After calcination, the CNTs supported catalysts were in situ sulfurized in a fixed bed reactor. Typically, Ni-Mo/CNT catalyst was packed into a stainless steel tube, then the sulfurizing agent (cyclohexane solution containing 5% CS_2) was pumped into the catalyst bed and the sulfurization process was carried out at 400 °C in 2.0 Mpa H_2 for 5 h with a weight hourly space velocity (WHSV) of 37.44 h^{-1} and a H_2/feed ratio of 250:1 (v/v). After sulfuration, the catalyst bed was cooled to room temperature in N_2 to prevent oxidization, and the product was marked as Ni-Mo-S/CNT. Other catalyst precursors were treated with the same procedure and the products were termed as Mo-S/CNT, Ni-S/CNT and Ni + Mo-S/CNT respectively.

2.2. Computation models and methods

The calculations were performed using the Vienna ab-initio simulation package (VASP), where the electron-ion interaction was described by the projector-augmented wave (PAW) method [22,23].The exchange-correlation functional with generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE) was applied [24]. The plane-wave cut off energy of 400 eV was set for all calculations. During the geometry optimization, the convergence criterion for the self-consistent step was performed using a 10^{-5} eV threshold, and the tolerance of force was set to 0.02 eV/Å. The Brillounin zone was sampled using a Monkhorst-Pack k-point set of 2 k-points, 1 k-point and 1 k-point in the x-, y- and z-direction, respectively [25]. The Nudge Elastic Band (NEB) method was used to find transition states firstly [26]. Frequency calculations were performed finally to verify the transition states, all of the presented TSs had only one imaginary frequency.

In this work, MoS_2 edge plane, which was accepted as the active-site containing plane, was used as the catalyst model. It was a single-layer periodic stripe model consisting of four rows of four metal atoms with the Mo-edge (50% S coverage) and the S-edge (50% S coverage) as shown in Fig. 1. Subsequently, the model was rebuilt by replacing edge molybdenum atoms partially to nickel atoms on the sulfur edge to form a Ni-Mo-S phase. The atoms on the edges of the catalyst were relaxed, while others were fixed. A vacuum layer of 15 Å was inserted between the neighboring surface slabs in the z-direction.

2.3. Characterization

X-ray powder diffraction (XRD) patterns for the prepared catalysts were recorded using a D/max-2500 system with Cu Kα radiation (λ = 0.154 nm). XPS of the sulfided catalysts were obtained using an AXIS (KRATOS) equipped with a magnesium anode. The spectra were recorded at a chamber pressure lower than 10^{-8} mbar, and the binding energies of the samples were estimated using the C 1s line at 284.8 eV as a reference. The microstructures of catalysts were observed by transmission electron microscopy (TEM, Tecnai). High-resolution

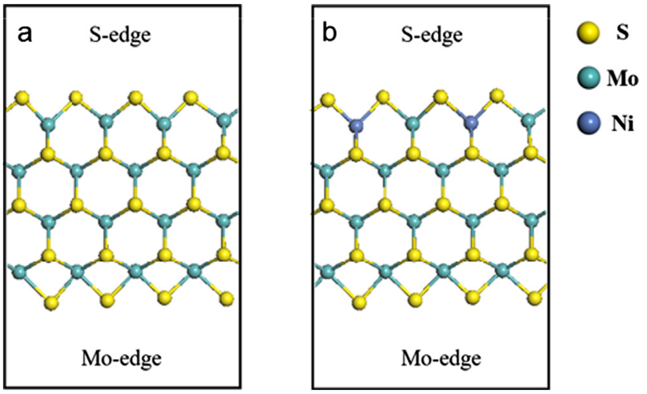

Fig. 1. Molecular model diagrams: (a) MoS_2, (b) Ni-Mo-S.

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